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SURFACE PROPERTIES OF GLASS MODIFIED WITH A NEW FROSTING PASTE. LIGHT SCATTERING IN THE SURFACE LAYER OF THE GLASS

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The results of an investigation of the optical properties of a 50-μm thick glass surface layer modified by a new frosting paste are presented. The action of the paste is based on a surface ion-exchange process that results in the formation of a system of microblocks and microcracks. The size distribution function of nonuniform scattering centers and the partial depolarization of the initially linearly polarized light are examined. It is noted that the light scattering characteristics of the modified glass layer are much different from the analogous characteristics of a glass surface which is frosted by chemical etching with a fluorine-containing etchant.

This present work is devoted to the investigation of light scattering in a nonuniform modified glass surface layer formed by working the glass surface with a new frosting paste (RF Patent No. 2238919).

In contrast to the chemical etching compositions the new paste for frosting glass (GFP) does not contain hydrofluoric acid or its derivatives. The action of the paste is based on a surface ion-exchange process [1 – 3]. This process proceeds at about 300°C; it is accompanied by the exchange of lithium ions, which diffuse from the bulk of the reaction paste mixture, for the sodium ions in the glass; and, it is characterized by a decrease of the volume of the product formed as compared with the volume of the initial glass. The shrinkage coefficient (ratio of the volume change in the course of the reaction to the initial volume of the glass in the reaction zone) is about 5%. The large shrinkage is the reason for the accumulation of mechanical stresses in the surface layer of the glass, which give rise to the appearance and propagation of microcracks.

The conditions for frosting the glass with the new paste and the electron-microscope data on the structure of the modified surface layer are presented in [4, 5]. The most important structural feature formed in the surface layer of the glass during the ion-exchange process is a system of microblocks and microcracks. The thickness of the modified layer depends on the conditions of the process (temperature, duration of the heating stage, the composition of the paste, and so forth). The experimental data testify to the large difference between such a structure of the surface layer of the glass and the surface morphology arising as a result of working the glass by well-known methods, such as sand blasting and chemical etching.

The formation of a nonuniform, modified structure of the surface layer of the glass could result in a large change in its physical properties, specifically, the structure-sensitive properties. The objective of the present work is to investigate the optical properties of the glass with a modified surface layer structure, which determine the character of light scattering. It is also of interest to study the optical properties of glass samples with a structurally modified surface layer coated in vacuum with a thin layer of a metal, since metal-coated glass with a modified surface layer can have technical and decorative applications.

The properties of the modified surface layer were investigated for 4 – 6 mm thick samples of sodium-calcium-silicate glass (GOST 111–2001). The process resulting in the modification of the glass surface using GFP included the following steps (RF Patent No. 2238919) [5]:

degreasing of the surface and washing in warm running water;

deposition of a layer of paste on the glass surface, using a silk stencil mold or a stencil (ORACAL Company) made by gluing a film;

removal of the stencil, if it was used at the preceding stage;

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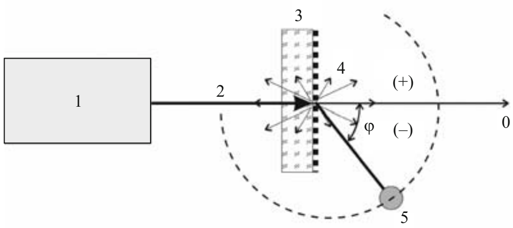

Fig. 1. Scheme used to measure the scattering phase function for monochromatic light: *1*) laser; *2*) direction of the light incident on the sample; *3*) glass sample with a modified surface (right-hand side); *4*) back-scattered light; *5*) photodetector; φ) light-scattering angle.

heat-treatment of the glass sample at 300°C for 15 – 20 min;

removal of the dry layer of paste by washing in warm running water.

In the case where a stencil with a glued film was used, the layer of paste deposited on the glass was about 50 μm thick.

The surface of the glass samples was chemically etched with a fluorine-containing paste, prepared according to the recommendations presented in the USSR Inventor's Certificate No. 948926 A, for frosting glass.

An about 10 nm thick layer of gold was pre-deposited in vacuum, using a JFC-1600 apparatus, on the glass samples for electron-microscopic studies of the glass surface (performed with a JSM-6460RV scanning electron microscope (Jeol, Japan). A 50 – 200 nm thick layer of gold was deposited to investigate the optical properties.

The following optical properties were determined: the scattering phase function of the light, the size distribution of the scattering centers (structural nonuniformities which form in the surface layer during surface treatment), the degree of the depolarization of the light, and the wavelength dependence of the intensity of the forward-scattered light. The optical properties were studied for samples with a GFP modified layer of glass, including with a thin layer of metal deposited on the glass. For comparison, glass samples whose surface was treated by chemical etching were also studied.

The detection scheme shown in Fig. 1 was used to measure the scattering phase function of the glass objects. Lasers (488-nm argon arc laser or 640-nm RLT6315G semiconductor laser) were used as the sources of the probe radiation. The laser beam was directed onto the unfrosted surface in a direction normal to the surface. The light scattered by the sample was detected with a photodetector secured to a mobile console. The rotation axis of the console passed through the point of incidence of the beam on the scattering surface. The dashed curve depicts the trajectory of the photodetector during the measurement process. The scattering angle φ was measured relative to the direction of the laser beam (the sign of the angle is shown in the diagram). The direction 0° corresponds to forward scattering; backscattering corresponds to – 180° (toward the laser). A two-channel detector was used to measure the signal from the sensor and the position angle of the sensor simultaneously.

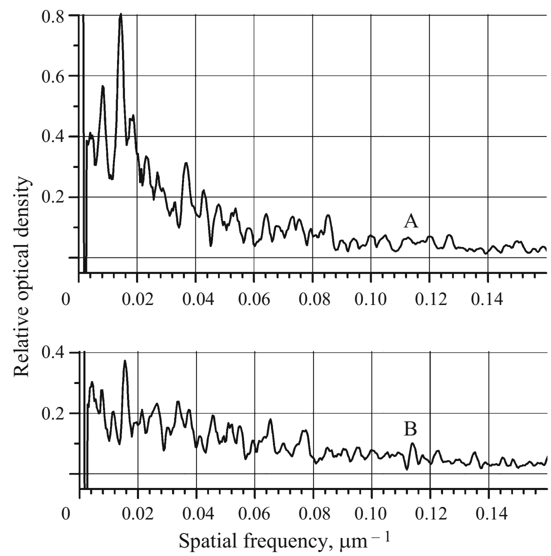

Fig. 2. Relative optical density of the scattering centers (samples A and B) versus their size.

The character of the size distribution of the scattering centers, which is due to the structural nonuniformities formed in the surface layer of the glass at the time the surface is worked with the GFP or a chemical etchant, also determines the light scattering by the glass surface. This distribution was calculated by Fourier analysis of the optical density distribution, whose digital values were determined by means of microphotography of the surface of the sample along a selected direction. Transmission optical microscopy with × 60 magnification was used to obtain photomicrographs of the image of the scattering centers of the glass objects. The size spectrum of the scattering particles of the glass sample characterizes the dependence of the optical density on the reciprocal spatial frequency (Fig. 2). The lineal size of the scattering centers was calculated as the reciprocal of the spatial frequency. Thus, 10-μm scattering centers correspond to the spatial frequency 0.1 μm^{-1}.

The degree of depolarization for forward scattering was determined for linearly polarized light with wavelength 488 nm by measuring the intensity of the light passing through a polaroid versus the angle of rotation φ of the polaroid. Since the initial laser light is linearly polarized, for a crossed arrangement of the polaroid, corresponding to 90°, the light is completely absorbed by the polaroid. Consequently, for linearly polarized light the plot of the angular dependence of the transmitted radiation is a half-period of the function $\cos^2 \varphi$. For unpolarized light, the intensity of the transmitted light is independent of the position of the polaroid. The light scattered by the experimental glass samples was partially polarized.

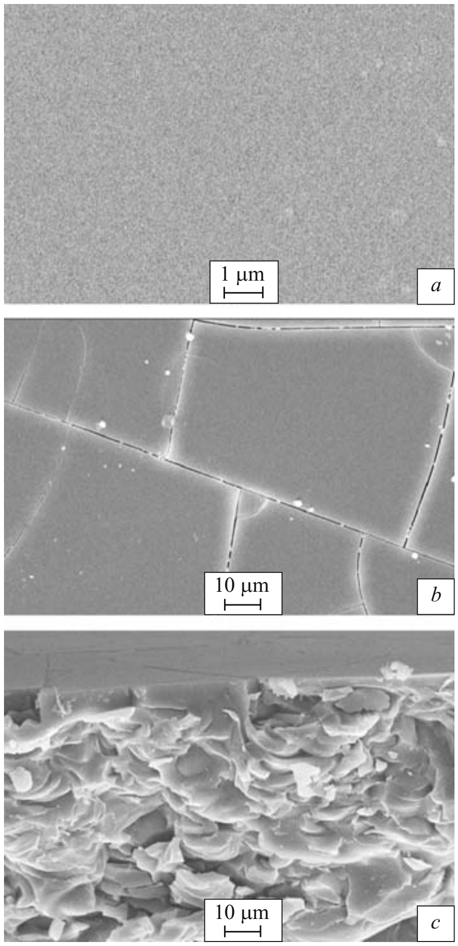

Fig. 3. Electron-microscope photographs of the glass surface: *a*) unworked surface; *b*) after working with GFP; *c*) same in a transverse section.

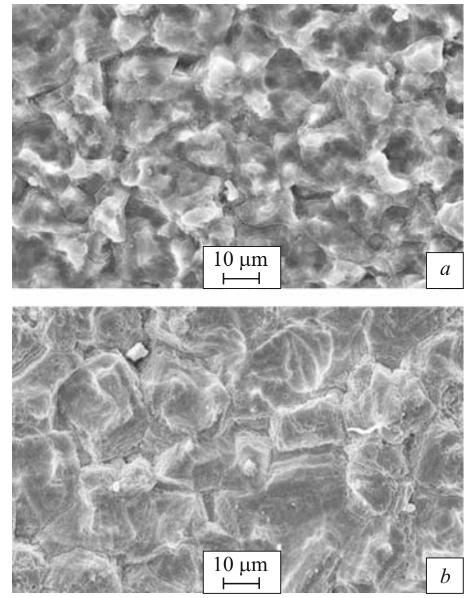

Fig. 4. Electron-microscope photographs of the glass surface after chemical etching: *a*) without deposition of gold; *b*) with subsequent deposition of a 50-nm thick layer of gold.

A polarization microscope was used to determine the optical activity of the glass samples in white light.

Microrelief of a Glass Surface. Since the optical properties of glass which we are studying depend strongly on the structure of the modified surface layer, we shall briefly discuss the particularities of this structure. If the untreated glass surface is essentially smooth right up to substantial magnification (Fig. 3*a*), then the structure of the surface of the glass with a modified layer formed after working with GFP is characterized by a system of microblocks and microcracks (Fig. 3*b*).

As already noted, the appearance of such a structure is due to surface exchange of Li^+ ions in the paste for Na^+ ions. This process is characterized by a decrease of the volume of the product formed, which leads to the accumulation of mechanical stresses in the surface layer of the glass and to the appearance and propagation of microcracks. The quite complex structure of the modified surface layer of the glass is shown in a transverse section in Fig. 3*c*.

The structure of the modified surface layer of glass differs substantially from the structure of a glass surface which has been subjected to chemical etching (Fig. 4). In the latter case chemical etching is accompanied by the removal of components of the glass with different rates on different sections of the surface with the formation of a microrelief with pits and bumps; the process does not penetrate into the interior volume of the glass.

The surface structure arising on the glass after working with GFP or after chemical etching, followed by vacuum deposition of thin layer of gold with different thicknesses, on the whole reflects the surface structure formed on the glass before deposition of the metal (Fig. 5). The particularities consist in the deposition of gold on the boundaries of microblocks and small crystalline nuclei of the gold on the front meal-coated surface, and this effect intensifies with increasing thickness of the coating.

Optical Properties of a Modified Glass Surface. Surface modification of glass using the new frosting paste, just as frosting by chemical etching and sand blasting, finds wide application, since one of the most important properties of glass which are used in practical applications (engineering and design) are not only transparency but also the scattering power. In the present work we measured the optical characteristics of a glass surface layer modified by GFP (samples A). For comparison, similar measurements were performed for a glass surface worked by chemical etching (samples B).

For the A samples, a maximum of the average relative optical density of the reciprocal spatial frequency range $0.01 - 0.02\ \mu m^{-1}$, which corresponds to $50 - 100\ \mu m$ scattering structural nonuniformities in the surface layer and correlates with the lineal sizes of the microblocks of the modified surface layer of the glass, is characteristic. The relative optical density decreases with increasing reciprocal spatial

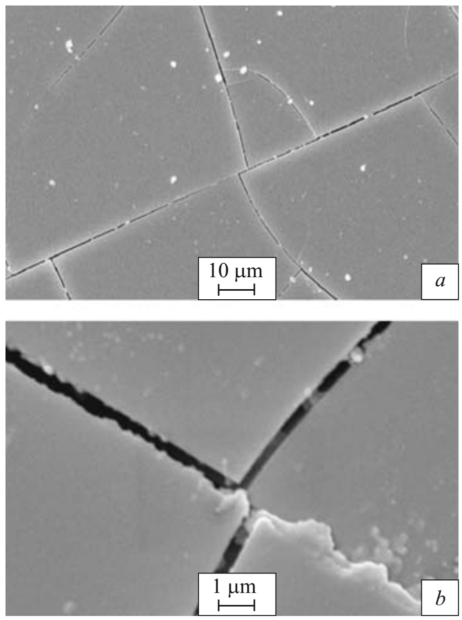

Fig. 5. Electron-microscope photographs of the surface layer of the glass after working with the GFP and subsequent deposition of 50 nm (a) and 200 nm (b) thick layers of gold.

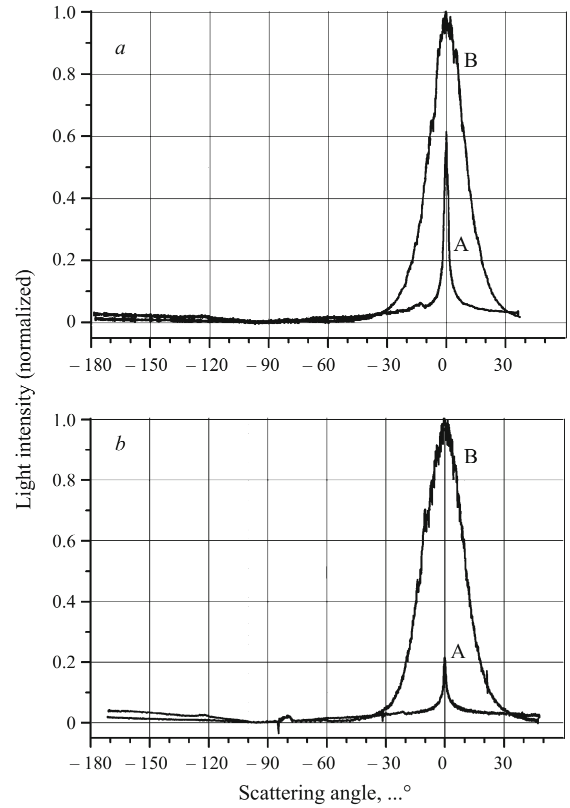

Fig. 6. Scattering phase functions for monochromatic light with wavelength 640 nm (a) and 488 nm (b) for the A and B samples.

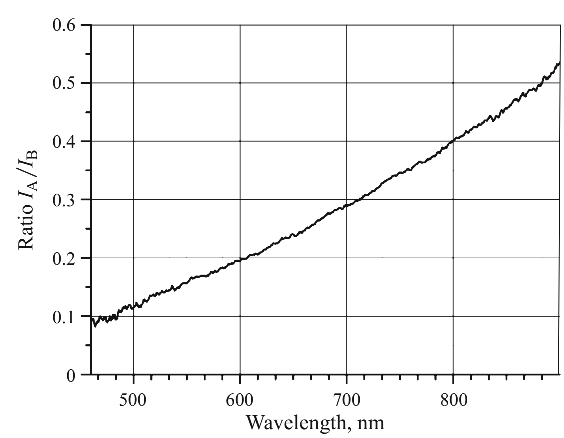

Fig. 7. Spectral curve of the intensity ratio of forward-scattered light for the A and B samples.

frequency (> 0.04), i.e., structural nonuniformities with lineal size < 25 μm have only a negligible effect on the size distribution of the scattering centers.

The relative optical density of the B samples decreases monotonically with increasing reciprocal spatial frequency. This shows that as the scattering structural nonuniformities in the surface layer decrease in size, the contribution of the size distribution function decreases. In this case a maximum is not observed on the optical density curve.

The light scattering phase functions are presented in Fig. 6. For samples with a GFP modified surface layer of glass, characteristically, scattering is weak and the scattered light is narrowly directed in the forward direction as compared with chemically etched samples. For the B samples, the half-width of the scattering phase function is about 10° for red light (640 nm) and about 15° for blue light (488 nm), while the half-width of the forward-scattering phase function for the A samples is much smaller and comparable to the angular divergence of the laser beam. Measurements of the half-width of the scattering phase function were problematic for the A samples, since the intensity of the light after transmission precisely in the forward direction was actually substantial and required screening the precisely forward-scattered beam in order to prevent malfunctioning of the photodetector.

The spectral dependence of the intensity ratio of the forward-scattered white light of the A and B samples is displayed in Fig. 7. An incandescent lamp was used as the light source. Sample A scatters light more strongly, and its relative scattering power increases appreciably with decreasing wavelength. This is a consequence of the differences in the structural nonuniformities for sample A as compared with sample B. Comparing Figs. 3a and 4a shows that the worked layer of sample A contains a large number of fine nonuniformities with sharp edges. This gives rise to scattering of light as a result of its diffraction by the edges. The diffraction angle is

$$\theta \approx \lambda/d,$$

where λ is the wavelength of the incident light and d is the size of a scattering center.

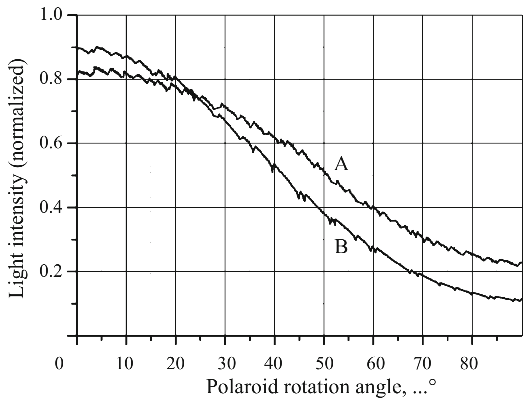

Fig. 8. Degree of depolarization of the forward-scattered monochromatic light (488 nm) in the A and B samples.

In this connection, as a result of the diffraction, the scattering centers must be of the order of the wavelength in size for light scattering to be effective. Specifically, diffraction by sharp vertices leads to scattering at short wavelengths. For the B sample, the surface microrelief is comprised of pits with smooth boundaries; it is these pits that serve as scattering centers. Such a structure of the scattering centers with smooth boundaries results in a lower scattering efficiency in the short-wavelength region of the spectrum. Sharp oscillations of the curve in the short-wavelength range are due to the small signal/noise amplitude ratio, since the intensity of light at wavelengths less than 500 nm, emitted by the lamp, is low.

Aside from scattering by structural nonuniformities of the surface layer, partial depolarization of the light can also occur. The degree η of depolarization gives the ratio of the intensity $I_\perp$ of the light polarized in a direction perpendicular to the initial light to the intensity $I_\parallel$ of the light retaining its initial (parallel) polarization [6]:

$$\eta = I_\perp / I_\parallel .$$

Curves of the light intensity versus the rotation angle of the polaroid for the A and B samples are displayed in Fig. 8. Partial depolarization of the initial linearly polarized laser beam is observed in both cases, but the depolarization of the light for samples with a GFP modified surface layer (sample A, $\eta_1 = 0.27$) is greater than for chemically etched samples (sample B, $\eta_2 = 0.12$), which is expressed at a deeper modulation of the radiation in the case of the A samples.

It was of interest to investigate samples for optical activity, since this optical characteristic can attest to the presence in glass of stressed regions which are visible in polarized light. However, for the A and B samples there were no indications of optical activity that would manifest in the appearance of colored regions in a visible microscopic picture obtained with a polarization microscope in white light.

Optical Properties of a Modified Glass Surface Coated with a Thin Layer of Gold. GFP modified glass, just like glass frosted by conventional methods (chemical etching or sand blasting) could be of practical interest in cases where the surface of the glass is coated with a thin layer of metal and where the glass is used in reflected light.

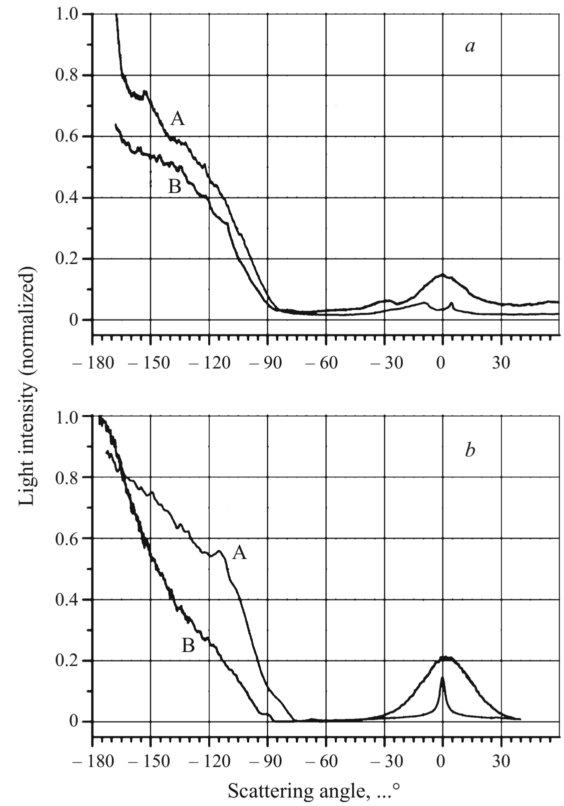

Fig. 9. Scattering phase functions for monochromatic light with wavelength 640 nm (*a*) and 488 nm (*b*) for A and B samples with a gold coating (50 nm).

The scattering phase functions obtained for the A and B samples coated with a thin layer of gold are presented in Fig. 9. As a result of the high reflectivity of the layer of metal, the scattering phase function of the A and B samples differs substantially from that of the uncoated samples (see Fig. 6). In the present case, a wide backward-scattering phase function is observed (scattering angles from – 90 to – 180°). It should be noted that for sample A a narrow light-scattering peak at small angles and a wider scattering phase function as compared with sample B are characteristic. At the shorter wavelength (488 nm) the back-scattering intensity increases at smaller angles ($\varphi \sim 60 - 70°$) than for the light with the longer wavelength (640 nm, $\varphi \sim 90°$).

Apparently, the broadening of the back-scattering phase function of the metal-coated A sample is due to the presence of the microstructure of the modified layer with fragmentation blocks which are predominately 100 – 200 μm in size, according to the data from electron microscopy and the data on the size distribution of the scattering centers, and are oriented at different angles. When thin gold layers are deposited, the microstructure of the modified surface layer con-

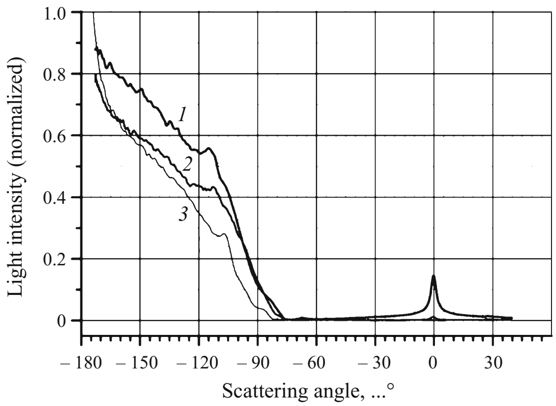

Fig. 10. Light (488 nm) scattering phase functions for GFP-treated samples and after deposition of a gold layer with thickness 50 nm (*1*), 100 nm (*2*), and 200 nm (*3*).

sists of numerous randomly oriented reflecting particles. In practice, this means that a reflective metallic coating deposited on a modified surface of glass will be visible at large angles.

In the case of a chemically etched glass surface, only a surface microrelief which does not extend into the interior of the surface layer of the glass is present. Consequently, back-scattering of light is first observed at $\varphi \sim -90°$.

The character of the scattering phase function of the A samples changes as the thickness of the thin gold layer increases (Fig. 10). The sample with the thinnest metal layer possesses the best reflecting and scattering properties. This is probably due to the weaker absorption of light by the layer of metal and preservation of the micrononuniformities at the scattering surface. For thicker gold layers, the nonuniformities become smoothed because the metal coating partially heals the microcracks, the reflection of the metal-coated surface layer intensifies, and light transmission sharply decreases.

In summary, the structural particularities of a glass surface layer modified with a new frosting paste have the effect that the light scattering characteristics of this surface layer differ substantially from those of a surface layer of smooth glass as well as chemically etched glass. In addition, stronger depolarization of the linearly polarized light and a wider back-scattering phase function are characteristic for such a modified surface layer in the presence of a thin metal coating (50 – 200 nm).

Glass worked with the new frosting paste is promising for use as a substrate for functional coatings (photoelectronics, electronics, decorative treatment of glass and coatings on glass).

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